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<p>(54) Title: CATALYST, PROCESSES AND POLYMER PRODUCTS THEREFROM</p>			
<p>(57) Abstract</p> <p>A cobalt/aluminum catalyst for the polymerization of polyesters of terephthalic acid and an ethylene glycol, a process for the preparation of such catalysts, a process for the polymerization of terephthalic acid and an ethylene glycol, a process of spinning fibers of such polyesters where reduced spinneret wiping is achieved, and fibers of such polyesters containing catalyst residues of cobalt/aluminum, and films or bottles of said polyesters.</p>			

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TITLECatalyst, Processes and Polymer
Products Therefrom

5

This invention relates to a catalyst useful for the preparation of high molecular weight polyester polymers of terephthalic acid and ethylene glycol, to the process for the production of such high molecular weight polyester polymers, to such high molecular weight polyester polymers made by the process using the catalyst, and to products made from such polyester high molecular weight polymers such as fibers, films, and bottles.

15

Many commercial processes for the production of high molecular weight polyester polymers of terephthalic acid and ethylene glycol employ an antimony catalyst. The use of an antimony catalyst presents some problems when the polymer is melt spun into fibers, i.e., the antimony catalyst residues form deposits around spinneret holes. These deposits must be wiped off from time to time or the filaments will be defective. It is believed that the antimony deposits form because antimony is present in the polymer as antimony glycolate, which boils at about the temperature of the spinneret. The antimony glycolate vaporizes, and then hydrolyzes, leaving a non-volatile antimony containing deposit at the spinneret. A non-antimony containing catalyst is, therefore, a desirable goal.

25

High molecular weight polyester polymers of terephthalic acid and ethylene glycol are usually produced by one of three different processes, namely, (1) the direct esterification and then polymerization of pure terephthalic acid and ethylene glycol. (This direct polymerization process is satisfactory only if the ingredients are of high purity.) (2) Transesterification of dimethylterephthalate (DMT) and

ethylene glycol to form, what is called in the art, "DMT monomer." The transesterification usually takes place in the presence of a manganese, zinc, or lithium catalyst. The DMT monomer is a mixture of ester products (low molecular weight polymer) in which most of the end groups are glycoxyl, and the mixture contains molecules with a degree of polymerization that is 1, 2, or 3. The DMT monomer is then further polymerized to high molecular weight polymer often with an antimony catalyst. The manganese catalyst used in the transesterification reaction tends to cause undesirable color in the final product unless it is sequestered; so phosphorus compounds, for example, H_3PO_4 , are often added before the DMT monomer is polymerized to sequester the manganese catalyst residue. (3) Reaction of medium purity (polymer grade) terephthalic acid and ethylene glycol to form, what is called in the art, "oligomer." The oligomer mixture contains color forming catalyst residues from the manufacture of terephthalic acid. These catalyst residues include manganese, iron, and molybdenum. These catalyst residues are then sequestered by the addition of a phosphoric compound, for example, H_3PO_4 , and then polymerized (polycondensed) to form high molecular weight polymer. The oligomer has a degree of polymerization of about 7, has 500 to 1000 carboxyl end groups per 10 to the 6th power grams of oligomer. Some cyclic materials are present in the oligomer. (This third process does not require the highly purified starting materials necessary for the first process described above.) The catalyst of the invention is useful in all three of these processes. In the first process described, the catalyst of the invention may be added at the direct esterification step or at the beginning of the polymerization; in the second process described, the catalyst will be added after the DMT monomer is formed and after the manganese catalyst is sequestered (deactivated); and in the third process the

catalyst will be added after the color-forming metal impurities in the oligomer are deactivated.

Combinations of metals compounds have been employed in the prior art as catalyst for the

5 preparation of high molecular weight polymers of terephthalic acid and ethylene glycols: see, for example, Nichols U.S. Patent 5,116,311; Engle-Bader et al. U.S. Patent 5,166,938; and Kosky et al. U.S. Patent 4,590,259.

10 The present invention is a polymerization catalyst useful for the preparation of high molecular weight polymers of terephthalic acid and ethylene glycol comprising a cobalt salt and an aluminum compound selected from the group consisting of
15 aluminum chloride, aluminum hydroxide, aluminum acetate, and aluminum hydroxychloride dissolved in ethylene glycol, where the mole ratio of aluminum to cobalt is 0.25 to 1 to 16 to 1, and where the mole ratio of chlorine to aluminum is in the range of 0 (no
20 chlorine) to 3 to 1.

The present invention is also a process for the production of ethylene terephthalate polyester polymer, which comprises combining a polymerization catalyst formed by combining a cobalt salt that is
25 soluble in ethylene glycol and aluminum compound selected from aluminum chloride, aluminum hydroxide, aluminum acetate, and aluminum hydroxychloride in ethylene glycol, where the mole ratio of aluminum to cobalt is 0.25 to 1 to 16 to 1 and a chlorine to
30 aluminum ratio in the range of 0.25 to 3 with (a) terephthalic acid and ethylene glycol, or (b) low molecular weight ethylene terephthalate polymer (also called DMT monomer), or (c) oligomer, where the concentration of cobalt in the thus formed mixture is
35 in the range of about 10 to 100 parts per million parts of the mixture, and polymerizing the mixture. The aluminum to cobalt mole ratio may be in the range of 1 to 1 to 16 to 1 in some circumstances. The optimum

aluminum to cobalt mol ratio for good polymerization and color is about 0.67.

Useful cobalt salts include cobaltous acetate tetrahydrate, cobaltous nitrate, cobaltous chloride, 5 cobalt acetylacetone, cobalt napthenate, cobalt hydroxide, and cobalt salicyl salicylate. The preferred cobalt salts are soluble in ethylene glycol in the 100-10,000 parts per million cobalt range.

This invention is also a process for the 10 preparation of a catalyst for the preparation of ethylene terephthalate polyester polymer, which comprises heating a cobalt salt and aluminum compound selected from the group consisting of aluminum chloride, aluminum hydroxide, aluminum acetate, and 15 aluminum hydroxychloride in ethylene glycol to a temperature in the range of about 40 to 180 degrees C where the aluminum to cobalt mole ratio is in the range of 0.25 to 1 to 16 to 1. A temperature range of about 40 to 180 degrees C is satisfactory: lower 20 temperatures lead to less corrosion of equipment when chloride is present with the aluminum or cobalt salts.

This invention is also an ethylene terephthalate polyester polymer having a NLRV of at least 12 and containing catalyst residues of cobalt and 25 aluminum; in other words derived from cobalt salt(s) and from aluminum chloride and/or aluminum hydroxychloride. The polymer can be in the form of a fiber or film or bottle.

This invention is also a process for the 30 production of ethylene terephthalate polyester polymer fiber in which there is a reduced need to wipe antimony deposits from the spinneret face which comprises melt spinning a molten mixture of ethylene terephthalate polyester polymer containing catalyst residue of cobalt 35 salt and an aluminum compound selected from the group consisting of aluminum chloride and aluminum hydroxychloride.

Detailed Description

When the catalyst of the present invention is used to prepare polyester polymer from polymer grade terephthalic acid or high purity terephthalic acid, the 5 terephthalic acid (TPA) and ethylene glycol will be fed into a reactor. The reaction to form oligomer will proceed without catalyst and is usually conducted at a temperature of about 240 to about 300 degrees C and at a pressure of about 0 to 50 pounds per square 10 inch (0 to 3.5 Kg/sq cm). Usually, the reactor will be fed more than an stoichiometric amount of the ethylene glycol, and the excess glycol separated by distillation. To the oligomer stream may then be added coloring agents such as carbon black, delustrants, 15 opaquing agents, color, and thermal stabilizers, copolymerization additives such as glycol esters of sodium or other metal dimethyl isophthalate-5-sulfonate, isophthalic acid, trimellitic acid and the like. Titanium dioxide is a conventional additive; it 20 serves as a whitening agent and a delustrant. Most commercial grades of titanium dioxide that are used in polyester fiber contain antimony compounds which serve as thermal and ultraviolet light stabilizers; so if titanium dioxide is added to the oligomer, the final 25 product will still contain some antimony, and antimony will show up in the analysis of the polymer. The antimony in the TiO_2 is chemically bound in the TiO_2 crystal. Since polymer grade TPA and plant grade ethylene glycol contain various amount of metals, for 30 example, iron, titanium, molybdenum, cobalt, and manganese, that tend to give color to the final product, a phosphorus compound, such as orthophosphoric acid, is often added to TPA/glycol slurry that feeds the direct esterfier or to the oligomer line and mixed 35 to sequester these color forming metal impurities. Then the catalyst of the present invention is added to the oligomer stream, and the oligomer is then subjected to polycondensation in the usual manner.

When the catalyst of the present invention is used to prepare polyester polymer from dimethylterephthalate (DMT), the DMT and ethylene glycol will be fed into a reactor along with a 5 transesterification catalyst, for example, manganese, zinc, or lithium acetates, or glycollates. The reaction that forms DMT monomer is usually conducted at a temperature of about 190 to about 260 degrees C and at a pressure of about 0 to 10 pounds per square inch 10 (0 to 0.7 Kg/ sq cm). Sodium or other metal dimethyl isophthalate-5-sulfonate may be added with the catalyzed glycol to make a copolymer. Methanol will be separated by distillation. To the DMT monomer stream may then be added fillers, coloring agents, such as 15 carbon black, delustrants, opaques, color, and thermal stabilizers, copolymerization additives such as glycol esters of sodium or other metal dimethyl isophthalate-5-sulfonate, isophthalic acid, trimellitic acid and the like. Titanium dioxide is a conventional 20 additive; it serves as a whitening agent and a delustrant. Most commercial grades of titanium dioxide used in polyester fiber contain antimony compounds which serve as thermal and ultraviolet light stabilizers; so if titanium dioxide (TiO_2) is added to 25 the DMT monomer, the final product will still contain some antimony, and antimony will show up in the analysis of the polymer. The antimony in the TiO_2 is chemically bound in the TiO_2 crystal. A phosphorus compound such as orthophosphoric acid is then added at 30 this point to (deactivate) sequester the ester exchange catalyst, for example, manganese compound. Then the catalyst of the present invention is added to the stream, and the DMT monomer subjected to polycondensation in the usual manner.

35 When the catalyst of the present invention is used to prepare polyester polymer from pure terephthalic acid, the terephthalic acid (TPA) and ethylene glycol will be fed into a reactor. The

reaction to form oligomer will proceed without catalyst and is usually conducted at a temperature of about 240 to about 300 degrees C and at a pressure of about 0 to 50 pounds per square inch gauge (0 to 3.5 Kg/sq cm).

5 Usually, the reactor will be fed more than a stoichiometric amount of the ethylene glycol, and the excess glycol separated by distillation. To the oligomer stream may then be added coloring agents, such as carbon black, delustrants, opaquing agents, color, 10 and thermal stabilizers, copolymerization additives such as glycol esters of sodium or other metal dimethyl isophthalate-5-sulfonate, isophthalic acid, trimellitic acid, and the like. Titanium dioxide is a conventional additive; it serves as a whitening agent and a 15 delustrant. Most commercial grades of titanium dioxide used in polyester fiber contain antimony compounds which serve as thermal and ultraviolet light stabilizers; so if titanium dioxide is added to the oligomer, the final product will still contain some, 20 antimony, and antimony will show up in the analysis of the polymer. The antimony in the TiO_2 is chemically bound in the TiO_2 crystal. Then the catalyst of the present invention is added to the oligomer stream, and the oligomer subjected to polycondensation in the usual 25 manner.

In order to be a viable replacement for the traditional antimony catalyst used to polymerize terephthalic acid/ethylene glycol polymers, the desired catalyst should meet the following criteria: 1. It is 30 preferably soluble in ethylene glycol, but some catalyst may be in slurry form, such as the reaction product of aluminum hydroxide and cobalt hydroxide. 2. It should produce a polymer which, when formed into a yarn, has a color, dyeability, and durability about as 35 good as the yarn made with antimony catalyst. 3. It should be capable of being used in the same equipment that is presently used for antimony catalyst. 4. It should have a reactivity as good as the antimony

catalyst. 5. it should not deposit on the spinnerets. 6. It should cost about the same as an antimony catalyst. 7. The catalyst residues should be not be toxic. The catalyst of the invention meets these 5 criteria.

The catalyst of the invention may be prepared as follows:

1. To a 500 cc agitated flasks with reflux condenser add:

10 0.64 grams of Cobalt diacetate. $4\text{H}_2\text{O}$ dissolved in about 209 grams of ethylene glycol at room temperature.

15 10.39 grams of Nalco 8676 (aluminum hydroxychloride) is then added with mixing. (Nalco 8676 has an aluminum to chlorine mole ratio of about 0.5. Nalco 8676 is a colloidal suspension in water of aluminum hydroxychloride particles. It is a 10% solution (based on Al_2O_3) of 20 nanometer particles.)

20 2. Heat 110 to 160 degrees C. and hold about 30 minutes. In ethylene glycol the solution turns from a pink to a deep purple. Then cool the catalyst solution. Analyses of the catalyst (Item 3 in the table below) indicated that the chlorine to aluminum mole ratio was about 0.5, and the aluminum to cobalt 25 mole ratio about 8 to 1.

Other catalysts were prepared by the above procedure and tabulated below.

TABLE OF POLYMERIZATION CATALYST SOLUTIONS

5	SAMPLE NO.	MOLS AL MOLS Co	GRAMS CoAc ₂ .4H ₂ O	GRAMS NALCO 8676	GRAMS OF ETHYLENE GLYCOL
	1	2	.64	2.57	216.8
	2	4	.64	5.14	214.2
	3	8	.64	10.3	209
	4	16	.64	20.6	198.8
10				GRAMS OF NALCO 8187*	
	5	4	.64	2.6	216.8
	6	8	.64	5.2	214
15				GRAMS OF AlCl ₃	
	7	2	.64	.686	218.7
	8	4	.64	1.372	218
	9	8	.64	2.744	216.6
	10	16	.64	5.489	213.9

20

*Nalco 8187 is aluminum hydroxychloride solution in water having an aluminum content measured as Al₂O₃ of 22% by weight.

25 (Nalco 8676 and 8187 were analyzed. The percent solids was determined by drying at 110 degrees C. Nalco 8676 was 21.9 +/- 1.6% solid, and Nalco 8187 was 46.2 +/- 0.39% solid. When calcined at 900 degrees C, Nalco 8676 was 9.75 +/- 0.23% solid, and Nalco 8187 was 22.6 +/- 0.05% solid. The aluminum content of Nalco 8676 was 5.68% by weight, and the chlorine content was 3.77%. The aluminum content of Nalco 8187 was 12.4%, and the chlorine content was 9.3%.)

30 To make polymer in a 1 liter resin kettle, add 400 grams of catalyst-free TPA oligomer. Add 8.6 grams of the catalyst solutions made per above table to the oligomer with ethylene glycol to make a 2/1 mole ratio of ethylene glycol/terephthalate. The total ethylene glycol and catalyst solution is 129 grams.

It is common commercial practice to vary the composition of polyester fibers by including, in the mixture to be, polymerized monomers that improve the dyeability of fibers made from the polymer. Sodium 5 isophthalic acid-5-sulfonate glycol ester or trimellitic acid glycol ester groups have often been incorporated in the polyester chains to improve dyeability. The catalyst of the present invention is compatible with making such copolymers.

10 The invention is further illustrated in the following polymerization Examples, all parts and percentages being by weight, except as indicated. NLRV and LRV are measures of relative viscosity, being the ratio at 25 degrees C of the flow times in a capillary 15 viscometer for a solution and for the solvent. The solution is 4.75 wt. percent of polymer in solvent. The solvent for NLRV is hexafluoroisopropanol. The solvent for LRV is hexafluoroisopropanol containing 100 parts per million H_2SO_4 .

20

Examples

25 **Example 1**
Lab Resin Kettle Example

Four hundred grams catalyst-free oligomer that was made from pure terephthalic acid and ethylene glycol was combined with 120.4 grams of ethylene glycol and 8.6 grams of ethylene glycol containing the 30 cobalt/aluminum catalyst (#3 in the above table). The amount of catalyst was such that the final polymer contained 14.8 parts per million cobalt, and 54 parts per million aluminum. The mixture was stirred at 60 revolutions per minute, heated to 265 degrees C for 30 35 minutes, to dissolve and remelt the oligomer into the glycol mixture, and then heated to 275 degrees C at a pressure of 120 millimeters of mercury and held at this condition for 20 minutes. The temperature was then

raised to 280 degrees C, and the vacuum adjusted to 30 millimeters of mercury and held at this condition for 20 minutes. Then the temperature was raised to 285 degrees, and the pressure lowered to about one (+/- 0.5) millimeters of mercury and held until the agitator torque reached 4 pounds per inch (71 Kg/meter) at 60 revolutions per minute. Then the agitator speed was lowered to 40 revolutions per minute, and the torque allowed to rise back to 4 pounds per inch. At this point, the polymer was cast in 1/2" (13 mm) wide strips in a pan of cold water. The polymer was then dried and crystallized at 90 degrees for one hour in a vacuum oven and then ground to pass through a 4 millimeters screen, and then the properties of the polymer determined. The polymer had an NLRV of 24.19, 26.5 COOH ends per 10^6 grams of polymer, 1.208% DEG (diethylene glycol), and a color on the Hunter scale L = 74.3, a = -0.5, and b = 6.8. The polymerization rate was about the same as that obtained with 200 part per million antimony; the color was close to that obtained from 200 part per million antimony, and the amount of diethylene glycol was somewhat higher than that obtained using 200 parts per million antimony, but still acceptable.

25 Similar Examples with other catalysts prepared, as shown in the "Table of Polymerization Catalyst Solutions," give similar results to this Example 1.

30 Example 2 and Control Examples Semi-Works Example

Control (Antimony Catalyst)

Dimethyl terephthalate (DMT) is fed at 84
35 pounds (38 Kg) per hour to plate 15 of a 20 plate ester
exchange distillation column. Catalyzed glycol was
made by dissolving 590 grams of manganese acetate with
4 waters of hydration, 115 grams of sodium acetate,

and 853 grams of antimony glycolate at about 50 degrees C in 1200 pounds (545 Kg) of ethylene glycol. This catalyst solution was fed at 210 milliliters/minute to plate 17 of the ester exchange column. Virgin glycol was fed to the calandria reboiler at about 70 milliliters/minutes to control the calandria temperature at 237+/-2 degrees C. Glycol boil up in the column was provided by Dowtherm® heat to the calandria's heat exchanger. Methanol was removed from the top of the column, and methanol reflux was provided to condense the glycol vapor. The monomer produced in the calandria was then pumped and filtered through a monomer line to the flasher. 13.8 milliliters/minute of 1% H₃PO₄ in glycol was added to the monomer line and mixed with the monomer to deactivate the ester exchange manganese catalyst. Then 9.5 milliliters/minute of 5% TiO₂ in glycol was injected into the monomer line and mixed with the monomer. The monomer was then prepolymerized in a Dowtherm®-heated flashing vessel operated at 245 degrees C and 90 millimeters of mercury pressure. The discharge from the flasher was fed to a Dowtherm® heated, agitated prepolymerization vessel operated at 275 degrees C and 30 millimeters of mercury pressure. The prepolymer from the prepolymerization vessel was then fed to a horizontal screen/wire filming agitated finishing vessel. This vessel was run at 285 degrees C and a pressure to produce 19.7 +/- 0.6 LRV. The polymer produced was pumped to a spinning machine where yarn was spun at 290 degrees C, quenched, and steam drawn to produce a 70 denier (78 dtex) 34 filament trilobal cross section yarn. This process and product properties will be compared with product made by use of the catalyst of the invention.

Dowtherm® is a registered trademark of the Dow Chemical Co.

Catalyst of the Invention with No Toner

The same process used to prepare the control yarn was used except, instead of dissolving antimony glycollate in the catalyzed glycol fed to the 5 exchanger, the cobalt/aluminum catalyst was prepared separately. 250 grams of cobalt acetate with 4 waters of hydration were dissolved in 180 pounds (82 Kg) of ethylene glycol. 4061 grams of Nalco 8676 was added, and the mixture was heated to 160 degrees C to form a 10 clear purple solution. This catalyst solution was injected into the monomer line at 24 milliliters/minute after the 11.4 milliliters/minute of 1% H_3PO_4 solution in glycol was added to deactivate the manganese catalyst.

15

Catalyst of the Invention with Toner

The catalyst was run the same way as described in the prior paragraph except 2 parts per million on a polymer basis of carboxyl violet was added 20 with the TiO_2 to change the hue color of the fiber.

TABLE: results of the control and invention catalyst runs.

		Without		
		Control	Toner	With Toner
5	Finisher pressure, mm Hg	2.96	2.88	3.02
	%DEG, analyzed	0.9	0.83	0.87
	%TiO ₂ , analyzed	0.096	0.097	0.093
	Sb analyzed, ppm	240	<1	<1
	Cobalt added, ppm	0	24	24
10	Mn, added, ppm	98	98	98
	Toner added, ppm	0	0	2
	Tenacity, gpd (g/dtex)	3.95(3.6)	3.9(3.5)	3.95(3.6)
	Elongation at break, %	32	33.4	33.4
	Boil off shrinkage, %	8	7.7	7.9
15	Draw tension, grams	105	104	103
	(1.2X Draw ratio, 185°C, 150 ypm = 137 mpm)			
	Glf dye	109	108	103
	Tube color, Hunter lab			
	L	84.7	83.3	82.3
20	b	1.2	2.5	1.15
	Color cards, Hunter lab			
	L	89.4	87.4	87
	a	-.62	-.38	-.13
	b	.74	2.10	.76

25

No visual difference could be seen between control and invention catalyst run with toner.

There was no significant change in spinning filter pack pressure rise rate.

30

Invention and control yarns were judged equal in physical properties.

Invention yarn without toner was less white.

Example 3
Semi-Works

Draw Textured Feed Yarn Example Made with TPA Process

5 Control Example

Oligomer, with about 7 average degrees of polymerization, was made in a commercial direct esterfier reactor. A side stream was pumped to the semi-works' flashing vessel, prepolymerizer, and 10 finishing vessels at 110 pounds (50 Kg) per hour. One item was made with no H_3PO_4 , and one item was made with 14 milliliters/minute of 0.1% H_3PO_4 that was injected into the oligomer line and mixed with a static mixer to deactivate color forming metal residues. Then 18.8 15 milliliters/minute of 1% antimony solution in ethylene glycol as the polymerization catalyst and 23 milliliters/minute of 10% TiO_2 , as the delustrant, was then added to the oligomer line and mixed with a static mixer. The polymer was spun through a filtration pack 20 and spinneret to produce a 265 denier (294 dtex) 34 filament draw textured feed yarn, known as partially oriented yarn (POY). This yarn was textured at 700 meters/minute on a Barmag FK-6-900 texturing machine.

25 Invention Example

The invention yarn was made in the same equipment, except that, instead of the antimony catalyst, 16 milliliters/minute of a cobalt aluminum catalyst solution was added to the oligomer line after 30 the H_3PO_4 was injected. This catalyst was made by dissolving 250 grams of cobalt acetate with 4 waters of hydration in 180 pounds (82 Kg) of ethylene glycol. Then 4061 grams of Nalco 8676 was added. The mixture was then heated with agitation to 170 degrees C 35 to produce a deep blue solution. The solution's theoretical cobalt level is 0.0725% and aluminum level is 0.263%.

Results comparing control and invention
product.

	Control	With	Invention
	Without H ₃ PO ₄	H ₃ PO ₄	With H ₃ PO ₄
5 Finisher pressure			
mm Hg	3.86	2.28	4.94
Sb ppm	228	217	39 (note 1)
TiO ₂ %	0.31	0.28	0.30
P ppm	4 (from TiO ₂)	9.5	10.1
10 COOH ends/10 ⁶ g	25	26	34
DEG%	1.15	1.12	1.31

Yarn properties

Draw tension, g	109.5	109	115
15 (185 degrees C, 1.71Xx draw ratio, 185 ypm = 169 mpm)			

Note: 1.9 parts per million antimony comes
from the antimony in TiO₂. About 30 parts per million
antimony is in the supply of oligomer.

20

Color on tubes

Hunterlab

	L	84.9	85.7	83.7
	a	-0.3	-0.3	0.4
25	b	1.9	1.14	0.9
	w	62.8	67.8	65.9

color on cards

	L	91.0	91.9	90.0
	a	-1.0	-0.85	-0.2
30	b	2.55	1.6	1.1
	w	69.5	76.1	75.3

	Tenacity, gpd (g/dtex)	2.47 (2.2)	2.44 (2.2)	2.43 (2.2)
35	Elongation, %	123.1	121.7	126.8

Colors of Control and Invention with H₃PO₄
were judged equivalent by visual examination.

The textured yarn results show:

	Control	With	
	Without H ₃ PO ₄	H ₃ PO ₄	Invention
5			
Tenacity, gpd (g/dtex)	4.37 (3.9)	4.19 (3.8)	4.21 (3.8)
Elongation %	22.38	21.06	21.17
Leesona shrinkage	18.2	20.0	17.9
10	(180 degrees F (82°C) in water, %		
% dye vs. std (100%)	101.1	103.1	102.1
Broken filaments	0.18 (0.40)	0.38 (0.84)	0
per pound (per Kg)			

15 Additional Examples

Similar polymerization experiments for the preparation of poly(ethylene terephthalate) polymer were carried out in which 0.83 mmoles of cobalt and 0.56 mmoles of aluminum were added to the mixture to be polymerized, using catalyst formed from cobalt diacetate and aluminum hydroxide, using catalyst formed from cobalt diacetate and aluminum triacetate and using catalyst formed from cobalt dihydroxide and aluminum hydroxide, and using catalyst formed from cobalt dihydroxide and aluminum triacetate in which 0.83 mmoles of cobalt and 0.28 mmoles of aluminum were added to the mixture to be polymerized, and using catalyst formed from cobalt diacetate and Nalco 8187 in which 0.84 mmoles of cobalt and 0.58 mmoles of aluminum were added to the mixture to be polymerized. The results were all highly satisfactory.

Claims:

1. A polymerization catalyst comprising a cobalt salt and an aluminum compound selected from the group consisting of aluminum chloride, aluminum hydroxide, aluminum acetate, and aluminum hydroxychloride in ethylene glycol, where the mole ratio of aluminum to cobalt is in the range of 0.25 to 1 to 16 to 1, and where the mole ratio of chlorine to aluminum is in the range from 0 to 3:1.
- 10 2. A process for the preparation of a catalyst for the preparation of ethylene terephthalate polyester polymer, which comprises heating a cobalt salt and aluminum compound selected from the group consisting of aluminum chloride, aluminum hydroxide, aluminum acetate, and aluminum hydroxychloride in ethylene glycol to a temperature in the range of about 40 to 180 degrees C where the aluminum to cobalt mole ratio is in the range of 0.25 to 1 to 16 to 1.
- 15 3. A process for the production of ethylene terephthalate polyester polymer which comprises combining a polymerization catalyst formed by combining a cobalt salt that is soluble in ethylene glycol and an aluminum compound selected from the group consisting of aluminum chloride, aluminum hydroxide, aluminum acetate, and aluminum hydroxychloride in ethylene glycol, where the mole ratio of aluminum to cobalt is 0.25:1 to 16:1, with terephthalic acid and ethylene glycol, or low molecular weight ethylene terephthalate polymer or oligomer, where the concentration of cobalt in the thus formed mixture is in the range of about 10 to 100 parts per million parts of the mixture and polymerizing the mixture.
- 20 4. A process according to Claim 3 in which the cobalt salt is selected from the group consisting of cobaltous acetate tetrahydrate, cobaltous nitrate, cobaltous chloride, cobalt acetylacetone, cobalt naphthenate, cobalt hydroxide, and cobalt salicyl salicylate.
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5. A process according to Claim 3, wherein sodium isophthalic acid-5-sulfonate glycol ester or trimellitic acid glycol ester is in the mixture to be polymerized.

6. A process for the production of ethylene terephthalate polyester polymer which comprises combining a catalyst solution in ethylene glycol having an aluminum to cobalt mole ratio in the range of 0.25:1 to 16:1 and a chlorine to aluminum mole ratio in the range from 0 to 3:1, with terephthalic acid and ethylene glycol, or low molecular weight poly(ethylene terephthalate) polymer or oligomer, where the concentration of cobalt in the thus formed mixture is in the range of about 10 to 100 parts per million parts of the mixture and polymerizing the mixture.

7. An ethylene terephthalate polyester polymer having a NLRV of at least 12 and containing catalyst residues of cobalt and aluminum.

8. A polymer according to Claim 7 in the form of a fiber.

9. A fiber according to Claim 8, that contains titanium dioxide and/or carbon black, and/or sodium isophthalic-5-sulfonate, and/or residues of a trimellitic acid glycol ester chain brancher.

10. A polymer according to Claim 7 in the form of a film.

11. A polymer according to Claim 7 in the form of a bottle.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 96/08484

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08G63/82

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G

Documentation searched other than minimum documentation is the same as that used for classification in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Character of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR,A,1 426 192 (TOYO RAYON KABUSHIKI KAISHA) 13 April 1966 see claims 1-4; examples 1-7 ---	1-11
A	US,A,3 533 973 (M. J. STEWART ET AL.) 13 October 1970 see claims 1-9 ---	1
A	EP,A,0 234 917 (CELANESE CORPORATION) 2 September 1987 see claims 1-6 ---	1,4
A	EP,A,0 399 797 (HOECHST CELANESE CORPORATION) 28 November 1990 see abstract; claim 1 -----	1,4

 Further documents are listed in the continuation of this C. Patent family numbers are listed in detail.

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1

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/08484

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
FR-A-1426192	13-04-66	GB-A-	1087552	
US-A-3533973	13-10-70	NONE		
EP-A-234917	02-09-87	CA-A- JP-B- JP-A- US-A-	1303771 6080109 62218417 4959445	16-06-92 12-10-94 25-09-87 25-09-90
EP-A-399797	28-11-90	US-A- CA-A- JP-A- JP-B-	4959449 2014746 3024125 7074267	25-09-90 25-11-90 01-02-91 09-08-95